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COMPLETE SPECIFICATION

Hair Dyeing and Bleaching Compositions

We, HANS SCHWARZKOPF, a German Company of 127—129 Hohenzollernring, Hamburg-Altona, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known to dye or bleach human hair using a paste or cream containing hydrogen peroxide, a thickener and an agent for controlling pH. Where a dyeing process is involved, the cream or paste also contains colour bases such as p-toluylene diamine, which undergo oxidation *in situ* to provide the dye colour. Such bleaching or dyeing compositions are usually made up shortly before use and have a pH greater than 7.0, a hydrogen peroxide concentration of 1.0 to 9.0% and a consistency such that they do not run off the hair after application. In the case of bleaching compositions persulphates are also frequently added to reinforce the bleaching action. In use the dyeing or bleaching cream is applied to the hair lock by lock, left to act for 20 to 30 minutes and then rinsed out.

It is also known to prepare powdered products containing all the substances necessary for oxidation dyeing, such as the colour base, oxidising agent, means for adjusting the pH, thickener, etc., which only need the addition of water to provide a ready-for-use composition. In such power compositions the oxidising agents used include sodium perborate and barium peroxide. However, these oxidising agents are only really effective as bleaching agents at temperatures above 60°C, which is too high for the dyeing of hair. Thus it is not possible with these oxidising agents to produce tints which are lighter than the original tint of the hair. In addition, the quality of dyeing at the roots of the hair, which is known to be a very important factor in assessing a dye, is unsatisfactory when

using oxidising agents such as sodium perborate. This is because although the oxidising agent can oxidise the colour base at an admissible temperature it is not capable of producing the necessary uniformity in bleaching the previous hair colour.

Hydrogen peroxide, which is conventionally used for dyeing and bleaching hair, is known to occur in solid form as an additive to urea (urea peroxide) but the use of urea peroxide in powdered hair dye compositions is unsatisfactory, since it is unstable in the presence of oxidation colour bases such as p-toluylene diamine. Mixtures of these bases with urea peroxide change colour in a few minutes. In the presence of salts which have an alkaline reaction in solution and which are often used for adjusting the pH of the dye cream, such as alkali carbonates and bicarbonates, decomposition of the urea peroxide adduct and a change in the colour of the base takes place almost instantly. The addition of hygroscopic salts such as sodium sulphate does delay decomposition but cannot prevent it. Since hydrogen peroxide is the most practicable oxidising agent so far known for dyeing and bleaching hair, it would be advantageous if a method could be found of stabilizing mixtures containing a colour base and a solid form of hydrogen peroxide such as melamine peroxide or urea peroxide.

In accordance with this invention, there are provided powdered dye and bleaching compositions comprising hydrogen peroxide or a solid adduct thereof and either an oxidative dye material capable of undergoing oxidation *in situ* on the hair to produce the dye colour or a material having an alkaline pH in water and present as a pH regulator for the bleaching composition, or a combination of such an oxidative dye material and a pH regulator, wherein said compositions are stabilised by microencapsulation of one or more of said ingredients by phase separation.

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Dyeing and bleaching powders in accordance with the present invention are stable and contain all the necessary materials such as thickeners, means for adjusting the pH, etc. and to which only water has to be added before use. Furthermore, all that is required to produce a dyeing or bleaching effect is to add water to the powder and work it into hair, or alternatively, to work the powder directly into wet hair. In order to increase the storage capacity of the dyeing or bleaching material still further it is an advantage also to microencapsulate the means for adjusting the pH, such as ammonium chloride and sodium carbonate. The pH regulator is preferably chosen so as to give a pH in the ready-for-use composition in the range 8.5—10.5.

Preferably the oxidative dye material is a polyaminobenzene, a polyhydroxybenzene, a polyhydroxyaminobenzene, a polyaminohydroxybenzene, a polyaminopyridine, a polyhydroxypyridine, a polyhydroxyaminopyridine, or a polyaminohydroxypyridine.

The dye and bleaching compositions may also contain a direct acting hair-dye material.

The encapsulating material used in accordance with the invention may, for example, be natural or synthetic polymers such as gelatin, casein, pectin, alginates, carboxymethyl cellulose, cellulose acetate, cellulose acetate phthalate, gum arabic, vinyl polymers such as polyvinyl acetate, or copolymers or different vinyl derivatives such as styrene, acrylic acid, acrylamide or acrylic esters which contain at least one polymer with a hydrophilic group such as the carboxy group or which, when dissolved, can form a hydrophilic group by hydrolysis. Microencapsulation may be carried out by the 'coacervation process,' either by using already pre-formed polymers or by using polymerisable monomers which are polymerised in the course of the encapsulating process.

The dyeing or bleaching powders may be used suspended in anhydrous cream bases which, when water is added or the cream applied to wet hair, form an oil-in-water emulsion with the water.

Examples of cream bases of this type are fatty alcohols such as cetyl alcohol and stearic alcohol, esters of fatty acids such as mono and diglycerides of fatty acids, oleyl esters of oleic acid, paraffins, natural waxes such as bees wax and carnauba wax, and modified natural waxes and completely synthetic ones, which may be used in combination with emulsifiers such as the monoethanolamide of stearic acid, salts of fatty acids and polyglycol ethers of fatty alcohols.

Bleaching powders can further be used suspended in an anhydrous but water soluble medium such as polyethylene glycol.

One advantage of using the powdered dyeing and bleaching material according to the

invention or suspension thereof is the fact that they are light to transport and that hydrogen peroxide solutions do not have to be transported with them; the use of hydrogen peroxide in glass bottles easily led to loss by breakage and where plastic bottles were used the solution frequently decomposed. The dyeing or bleaching powders may be dispatched, for example, as individual portion packs in plastic bottles or in long strings of linked plastic sachets.

In addition to the abovementioned compatibility between colour bases and oxidising agents and agents for adjusting the pH when microencapsulated products are used, a further advantage of microencapsulating urea peroxide or other hydrogen peroxide adducts such as melamine peroxide is the fact that the encapsulated peroxide adducts can be stored for long periods even at temperatures from 40 to 50°C without the slow decomposition which takes place with nonencapsulated peroxide adducts. Oxidation colour bases also gain improved storage capacity. Thus substances such as triaminobenzenes which change colour very readily by the action of the air may, for example, be stabilised against the action of atmospheric oxygen by microencapsulation.

The invention is illustrated by the following Examples. In these examples the hydrogen peroxide adducts and/or colour bases and/or means for adjusting the pH are microencapsulated by a coacervation process as follows: The encapsulating material, e.g. gelatin, is dissolved in an organic solvent system in which is suspended the material to be encapsulated, which is insoluble in the organic solvent. The suspension is stirred, its temperature is slowly raised and a petroleum distillate having a boiling point slightly above the temperature of the suspension is gradually added. This brings about the phase separation of the film former and of part of the original solvent system as a thick dispersed fluid. Once the encapsulating material has been deposited around the material to be encapsulated and the temperature has been lowered to room temperature the solvent in the dispersion is displaced by adding more petroleum distillate. The liquid is then decanted off. The non-adhesive microcapsules are rewashed several times and dried.

To the microencapsulated colour bases and/or the microencapsulated hydrogen peroxide adducts there are desirably added salts which may themselves be microencapsulated. The function of the salt is to ensure that when the powder is dissolved the aqueous dye paste or solution will have the desired pH. Examples of suitable salts are ammonium chloride and sodium carbonate. It is advantageous to use an ammonium salt and adjust the salt mixture so that when water has been added there is a defined quantity of free ammonia. Other solids which may be added are, for example,

thickeners, surface-active substances and stabilisers. Additives to modify the shade, such as dihydroxy benzenes or aminophenols may be added directly if they have sufficient stability in air, or otherwise they may also be used encapsulated. The said substances are mixed. The mixture may be applied either by applying the final dyeing or bleaching powder, or a suspension of the powder in an anhydrous cream base which gives an oil-in-water emulsion when water is added, or a suspension of the powder in an anhydrous but water-soluble medium consisting e.g. of polyethylene glycol directly to wet hair, or by first adding water to the powder or suspension before applying it to hair.

It is desirable to add a specific quantity of water to the powder or suspension before use. Once this has been done and the mixture briefly shaken or stirred, a paste ready for use is obtained. This is applied in the usual way and rinsed out after being left to act for 20 to 30 minutes. Furthermore, the dyeing or bleaching powder or its suspension in a cream base or in an anhydrous water-soluble solvent may be placed directly on the wet hair and rinsed out after acting on it for 20 to 30 minutes.

EXAMPLE 1

A powdered dye composition is made up containing the following ingredients, microencapsulation being done by the process described above:

4.500 g. p-toluylene diamine sulphate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 800 micron; content of p-toluylene diamine sulphate 3.800g);

0.950 g resorcinol;
0.420 g m-aminophenol microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 900 micron; m-aminophenol content 0.350 g);

0.250 g m-toluylene diamine microencapsulated in cellulose phthalate (capsule diameter 600 to 800 micron; content of m-toluylene diamine 0.210 g);

6.500 g polyacrylic acid, low viscosity;
0.150 g methyl cellulose;

14.150 g sodium carbonate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 1,000 micron; content of sodium carbonate 11.700 g);

7.850 g ammonium chloride microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 900 micron; content of ammonium chloride 6.500 g);

1.000 g sodium stearate; and
9.870 g urea peroxide microencapsulated in cellulose acetate phthalate (capsule diameter 400 to 1,300 micron; content of hydrogen peroxide 2.80 g).

Before use the composition is stirred into 100 ml water to form a spreadable paste. The

paste is then applied to the hair and after acting on it for 30 minutes results in black colouration. The hair is then rinsed, put into rollers, dried and set.

EXAMPLE 2

Similarly a powdered dye composition is made up from:

1.005 g p-toluylene diamine sulphate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 800 micron; content of p-toluylene diamine sulphate 0.850 g);

0.260 g resorcinol;
0.024 g m-aminophenol microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 900 micron; content of m-amino-phenol 0.020 g);

0.012 g m-toluylene diamine microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 800 micron; content of m-toluylene diamine 0.010 g);

6.500 g polyacrylic acid, low viscosity;
0.150 g methyl cellulose;

14.150 sodium carbonate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 1000 micron; content of sodium carbonate 11.700 g);

7.850 g ammonium chloride microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 900 micron; content of ammonium chloride 6.500 g);

1.000 sodium stearate; and
9.870 g urea peroxide microencapsulated in cellulose acetate phthalate (capsule diameter 500 to 1,300 micron; content of hydrogen peroxide 2.80 g).

When used in the manner described in Example 1, the dye composition produces a subdued brown tint.

EXAMPLE 3

Similarly, a powdered dye composition is made up containing:

0.946 g p-toluylene diamine sulphate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 800 micron; content of p-toluylene diamine sulphate 0.800 g);

0.200 g resorcinol;
0.024 g m-aminophenol microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 900 micron; content of m-aminophenol 0.020 g);

6.500 g polyacrylic acid, low viscosity;
0.150 g methyl cellulose;

14.150 g sodium carbonate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 1,000 micron; content of sodium carbonate 11.700 g);

6.500 g ammonium chloride;
1.000 g sodium searate; and
9.870 g urea peroxide microencapsulated in cellulose acetate phthalate (capsule diameter 500 to 1,300 micron; content of hydrogen peroxide 2.80 g);

When used in the manner described in

Example 1 the composition produces a deep blonde tone.

EXAMPLE 4

Similarly a powdered dye composition is made up containing:

- 0.178 g p-toluylene diamine sulphate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 800 micron; content of p-toluylene diamine sulphate 0.150 g);
 - 0.017 g resorcinol;
 - 0.020 g nitro-*p*-phenylene diamine;
 - 0.002 g nitro-*o*-aminophenol;
 - 6.500 g polyacrylic acid, low viscosity;
 - 0.150 g methyl cellulose;
 - 14.150 g sodium carbonate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 1,000 microns; content of sodium carbonate 11.700 g);
 - 6.500 g ammonium chloride;
 - 1.000 g sodium stearate; and
 - 9.870 g urea peroxide microencapsulated in cellulose acetate phthalate (capsule diameter 500 to 1,300 microns; content of hydrogen peroxide 2.80 g);
- Used in the manner described in Example 1 the composition dyes the hair blonde.

EXAMPLE 5

Similarly a powdered dye composition is made up containing:

- 1.600 g p-toluylene diamine sulphate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 800 microns; content of p-toluylene diamine sulphate 1.400 g);
 - 0.150 g resorcinol;
 - 0.200 g nitro-*p*-phenylene diamine;
 - 0.050 g nitro-*o*-aminophenol;
 - 6.500 g polyacrylic acid, low viscosity;
 - 0.150 g methyl cellulose;
 - 14.150 g sodium carbonate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 1,000 microns; content of sodium carbonate 11.700 g);
 - 6.500 g ammonium chloride;
 - 1.000 g sodium stearate; and
 - 9.870 urea peroxide microencapsulated in cellulose acetate phthalate (capsule diameter 500 to 1,300 microns; content of hydrogen peroxide 2.80 g);
- Used in the manner described in Example 1, the dye produces a chestnut brown tint.

EXAMPLE 6

Similarly a dye powder is made up containing:

- 0.946 g p-toluylene diamine sulphate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 800 microns; content of p-toluylene diamine sulphate 0.800 g);
- 0.650 g nitro-*p*-phenylene diamine;
- 0.040 g nitro-*o*-aminophenol;
- 6.500 g polyacrylic acid, low viscosity;
- 0.150 g methyl cellulose;
- 11.700 g sodium carbonate;

6.500 g ammonium chloride;
1.000 g sodium stearate; and
9.870 g urea peroxide microencapsulated in cellulose acetate phthalate (capsule diameter 500 to 1,300 microns; content of hydrogen peroxide 2.80 g);

Used in the manner described in Example 1, the composition produces a mahogany shade.

EXAMPLE 7

A hair bleaching powder composition is made up containing:

- 6.50 g polyacrylic acid, low viscosity;
- 0.15 g methyl cellulose;
- 27.20 g sodium carbonate microencapsulated in cellulose acetate phthalate (capsule diameter 600 to 1000 microns; content sodium carbonate 22.50 g);
- 13.00 g ammonium chloride;
- 1.00 g sodium stearate; and
- 14.80 g urea peroxide microencapsulated in cellulose acetate phthalate (capsule diameter 500 to 1,300 microns; content of hydrogen peroxide 4.20 g);

In order to use the composition it is stirred into 100 ml water to form a spreadable paste. This is applied evenly to the hair and left to act for 30 minutes. The hair is lightened by about three shades. When the 30 minutes have elapsed the paste is rinsed out and the hair is put into rollers, dried and set.

WHAT WE CLAIM IS:—

1. A powdered hair dye or bleaching composition comprising hydrogen peroxide or a solid adduct thereof and either an oxidative dye material capable of undergoing oxidation *in situ* on the hair to produce the dye colour or a material having an alkaline pH in water and present as a pH regulator for the bleaching composition, or a combination of such an oxidative dye material and a pH regulator, wherein said compositions are stabilised by microencapsulation of one or more of said ingredients by phase separation.

2. A bleaching composition according to Claim 1, comprising microencapsulate dhydrogen peroxide or a microencapsulated solid adduct thereof and a microencapsulated pH regulator.

3. A dye composition according to Claim 1, comprising microencapsulated hydrogen peroxide or a microencapsulated solid adduct thereof, a microencapsulated oxidative dye material, and a microencapsulated pH regulator.

4. A dye composition according to Claim 1 or Claim 3, wherein the oxidative dye material is one or more of the following a polyaminobenzene, a polyhydroxybenzene, a polyhydroxyaminobenzene, a polyaminohydroxybenzene, a polyaminopyridine, a polyhydroxypyridine, a polyhydroxyaminopyridine, or a polyaminohydroxypyridine.

5. A dye composition according to Claim 1, 3 or 4, also containing a direct acting hair dye material. 35
- 5 6. A composition according to any one of the preceding claims containing as the pH regulator ammonium chloride and/or sodium carbonate. 40
- 10 7. A composition according to any one of the preceding claims, containing microencapsulated urea peroxide and/or melamine peroxide. 45
- 15 8. A composition according to any one of the preceding claims, in which the encapsulating material is cellulose acetate phthalate.
- 20 9. A composition according to any one of the preceding claims, incorporated in an anhydrous cream base or in an anhydrous water miscible organic solvent.
10. Hair dye or bleaching compositions substantially as described in any one of the foregoing Examples.
11. A method of dyeing or bleaching hair that comprises applying to the hair in the presence of moisture a composition as claimed in any one of the preceding claims, allowing the composition to act on the hair, and then rinsing the hair and drying.
12. A method according to claim 11, in which the composition is premixed with water before application to the hair.
13. A method according to claim 11, in which the composition is applied directly to previously moistened hair.
14. A composition according to claim 1, substantially as hereinbefore described in any one of the foregoing Examples.
15. A method according to claim 11, substantially as hereinbefore described in any one of the foregoing Examples.

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